

Electronic-structure-induced deformations of liquid metal clusters

H. Häkkinen and M. Manninen

Department of Physics, University of Jyväskylä, P.O.Box 35, FIN-40351 Jyväskylä, Finland

(February 8, 2008)

Abstract

Ab initio molecular dynamics is used to study deformations of sodium clusters at temperatures $500 \cdots 1100$ K. Open-shell Na_{14} cluster has two shape isomers, prolate and oblate, in the liquid state. The deformation is stabilized by opening a gap at the Fermi level. The closed-shell Na_8 remains magic also at the liquid state.

Typeset using REVTeX

Electronic shell structure of alkali metal clusters has been established in numerous experiments (for a review see Ref. [1]). This shell structure corresponds to single-electron levels in a spherical potential and can be understood in terms of the simple jellium model [2]. It is also well-known that clusters with an open electronic shell are deformed from the spherical shape. In theory, the deformation has been extensively studied with jellium-type models [3–5], and it is also the result of ab initio calculations [6–8] and simple tight-binding models [9,10]. These calculations seem to indicate that the geometries of smallest clusters ($N < 20$) are determined solely by the symmetries of the single electron wavefunctions and are insensitive to the model. Moreover, even the small nuclei with equal number of nucleons seem to have the same geometries as alkali metal clusters [11,5].

The experimental information of the deformation is obtained from the intensity variation of the mass spectrum, or from the photoabsorption experiments [1] where the observed energies and the intensity ratios of the plasmon peaks are interpreted in terms of deformations of the valence electron distribution [12,13]. In these experiments the clusters are known to be hot, very likely liquidlike [14,15]. While the temperature can be incorporated in the electronic degrees of freedom of the jellium model [16], so far there has not been attempts to systematically study the interplay between the deformation of the ionic system and electronic structure at elevated temperatures by detailed dynamical simulations.

In this paper we report results obtained from ab initio molecular dynamics (MD) simulations of hot ($500 < T < 1100$ K) "magic" Na_8 and open-shell Na_{14} clusters. Our calculations confirm the magic nature of Na_8 by showing a large HOMO-LUMO gap in the proposed $T=0$ ground state geometry (dodecahedron) [7]. This gap remains clear also at $T \approx 550$ K, where the cluster is already liquidlike. In the open-shell Na_{14} the deformation opens a gap, which also remains in the liquid state. By studying the cartesian moments of inertia, calculated from the coordinates of ions, we show that Na_8 remains the most spherical of our clusters at high temperatures. In contrast, liquidlike Na_{14} cluster favour axially deformed (prolate and oblate) shapes, and the deformation of the ionic system is driven by the opening of the HOMO-LUMO gap, which is directly demonstrated by starting a simulation from a

practically spherical Na_{14} isomer.

Since the ab initio MD method we use is fully documented elsewhere [17], we only summarize here the key ingredients of our calculations. We perform the electronic-structure calculations in the framework of the density-functional theory, with the local density approximation for the exchange-correlation energy. The valence electron - ion interaction is described by norm-conserving pseudopotentials [19] with a plane-wave basis. For a given ionic configuration the Kohn-Sham one-electron equations are solved using an iterative matrix diagonalization scheme. From the converged solution, the Hellman-Feynman forces on the ions are calculated, and these forces together with the classical Coulomb forces between the positive ion cores determine the ion trajectories. We remark that due to the self-consistent solution of the electronic structure for each ionic configuration, the electrons are kept strictly on the Born-Oppenheimer potential energy surface, consequently, the length of the time step in the molecular dynamics simulation is limited only by the vibrational time scale of ions and the performance of the integration algorithm, just as in ordinary classical MD. In this study we use a fifth-order predictor-corrector algorithm with a time step of 5.2 fs, giving a good conservation of the (generalized) constant of motion in the MD simulation [18]. We also remark that the method does not employ periodic boundary conditions to the ionic system, i.e., no supercells are involved in the calculation. For that reason the method is particularly suitable for studies of finite charged or multipolar systems [17]. The calculations are performed typically on a cubic cell with a dimension of 45 a.u. and using a plane-wave kinetic energy cutoff $E_C = 4.4$ Ry. Test calculations using larger cutoffs up to 20.1 Ry show that by using $E_C = 4.4$ Ry the ionization potential of a sodium atom deviates 1 % from the converged value of 5.21 eV (experimental value 5.139 eV [21]), and the dissociation energy and bond length of sodium dimer are within 2 % and 5 %, respectively, from the converged values 0.82 eV and 2.98 Å (experimental values 0.80 eV and 3.08 Å, respectively [21]).

The initial configurations for the MD simulation are prepared by setting the ions to the desired geometry with a reasonable nearest-neighbour distance (≈ 3.5 Å) and optimizing the structure to a local minimum on the potential energy surface. We wish to emphasize here

that for our purposes it is not necessary to find an absolute global ground state, rather we wish to start the simulations from cluster isomers with representative electronic properties and (in the case of Na_{14}) desired deformations in the shape of the ionic configuration. For Na_8 , we consider only the dodecahedron. It has been found to be the ground state in previous pseudopotential-LDA calculations, where the ionic and electronic structure are optimized according to the Car-Parrinello scheme [7]. Our optimized dodecahedron has electronic properties very similar to those found in Ref. [7], showing a large gap of 1.1 eV between the highest occupied and the lowest unoccupied one-electron level. The angular momentum character of the four occupied levels is easily identifiable showing the lowest level to be s-type and the next three levels p-type, of which two higher ones are degenerate. The lower p-level is split from them by 0.4 eV and the gap between the s-level and the lowest p-level is 1.2 eV. Although a different structure (stellated tetrahedron) was found in all-electron configuration-interaction calculations [8], it has been shown [7] that all the low-lying isomers of Na_8 have similar electronic properties, and the cluster geometry we have selected serves well as an example of a magic cluster having a closed electronic shell. By looking at the principal moments of inertia, we find that two of them are degenerate and have a larger value than the third one, thus the cluster can be characterized as prolate, the ratio of the two values I_z/I_r (I_r degenerate, I_z non-degenerate moments) being 0.76.

We consider three isomers for Na_{14} , the shape of which can be characterized as prolate, oblate and "spherical". The prolate isomer has the lowest energy. Its geometry was chosen according to a recent study using Hückel method [10]. The cluster consists of three stacked squares, the middle one rotated 45° with respect to the others. The squares are capped by an atom at both ends of the long axis. The ratio I_z/I_r is 0.39. Of the seven occupied one-electron states, two lowest (identified as s and p) and two highest (d-type, degenerate) states show a single angular momentum component, the three middle ones having some degree of p-d mixing. The HOMO-LUMO gap is clear, 0.4 eV. The gap is greatly reduced for the two other isomers which results in a fractional occupancy around the Fermi level (see Ref. [18]). The geometric structure of the oblate isomer is obtained by relaxing two stacked hexagonal

layers of seven atoms (one atom in the middle), rotated 30° with respect to each other. It is interesting to note that the energy of this rather artificial structure is only 0.3 eV (or 0.02 eV/atom) higher than that of the prolate isomer. It is probable that we could find oblate isomers which are energetically even closer to the prolate isomer, paralleling the results of Lauritsch et al. [4], who find oblate and prolate shapes (of the electron density distribution) to be separated only by 0.1 eV in their jellium calculations for Na_{14} . Finally, the "spherical" isomer, having degenerate moments, is obtained by relaxing a structure where an atom is placed on one (100) face of the 13-atom cuboctahedron. The energy of the relaxed cluster is 0.9 eV higher than that of the prolate isomer. Looking at the electronic structure we find that the Fermi level lies in the middle of split 1d-levels, mixed with the 2s (according to the nomenclature in the spherical potential).

Next we follow the evolution of the geometric and electronic structure of each cluster in molecular dynamics runs, where the cluster is given enough kinetic energy to raise the (vibrational) temperature [22] to 500-600 K, after which the system is allowed to evolve at constant energy. The rapid heating results in a complete disorder (melting) during the first 1-2 ps, which is easily verified by monitoring the mean-squared displacements (msd) of atoms as a function of time. After the melting, a typical linear rise in msd versus time is observed, and the diffusion constant estimated from the slope of the msd curve falls in the range $(2 - 9) \times 10^{-5} \text{ cm}^2/\text{s}$, not far from the values $(9 - 13) \times 10^{-5} \text{ cm}^2/\text{s}$ expected for bulk liquid sodium at these temperatures [23].

The fluctuations of the geometric shape of the clusters are shown in Fig. 1, which shows the evolution of the three cartesian moments of inertia as a function of time, and in a two-dimensional "shape space", where a particular time step t_k is represented by a point $(I_1(t_k)/I_3(t_k), I_2(t_k)/I_3(t_k))$, where $I_1 < I_2 < I_3$. Trajectories in this space are confined within an upper-left triangle of a square, with corners of (0,0), (0,1), and (1,1). All the ideal prolate shapes ($I_1 < I_2 = I_3$) fall on the line (0,1)→(1,1) while the ideal oblate shapes ($I_1 = I_2 < I_3$) form the diagonal (0,0)→(1,1) of the square. The corner (1,1) obviously has all the shapes with degenerate moments, i.e. shapes which have at least the cubic symmetry.

As can be seen from Fig. 1a, the trajectory for Na_8 probes relatively uniformly the region around a triaxial average shape, characterized by coordinate (0.72,0.89). The evolution of the electronic structure is shown in Fig. 2a, where we plot the Kohn-Sham eigenenergies as a function of time. We see only minor changes compared to zero-temperature electronic structure: the HOMO-LUMO gap averages to 0.9 eV, and the splitting of the p-levels increases to 0.5 eV. It is interesting to note the survival of the zero-temperature gap also between the (unoccupied) 1d-2s manifold and the 1f levels (only two of them are plotted). This indicates that the average triaxial shape of the ionic configuration does not destroy too much the (approximately) spherical background potential felt by the electrons. The overall behaviour of the electronic shell structure confirms the magic nature of Na_8 even at $T=550$ K, in accordance with previous Car-Parrinello calculations [7].

We turn now to the more interesting case of the open-shell Na_{14} cluster (see figs. 1b-d and 2b-d). The results shown for the principal moments of inertia (Fig. 1b,c) for the runs starting from the prolate and oblate shapes show that both of these shapes are indeed stable (meaning that there is a marked energy barrier between them). Furthermore, transitions between isomers appear to be possible in the time scale of our simulations, $t \approx 10$ ps. (Fig. 1b). The gap visible at $T=0$ for the prolate isomer persists also in the finite-temperature simulation (Fig. 2b), and there is a gap opening for the oblate isomer as soon as the dynamics is turned on (Fig. 2c). It is instructive to note that even the Kohn-Sham eigenvalues reflect the shape of the cluster: for prolate shapes, the lowest p-type orbital (corresponding to the state along the longer axis) is separated from the higher p-orbitals whence for oblate shapes there is a gap between the two lowest (states along the two long axes) and the higher p-orbital. In both cases we observe a considerable mixing between the higher p-orbital(s) and the d-orbitals. Finally, Fig. 2d shows a "dynamical Jahn-Teller effect" taking place in the "spherical" isomer of Na_{14} . Within 0.5 ps after the dynamics is turned on, we see the splitting of the 1d-2s manifold and the gap opening at ϵ_F . The shape of the cluster deforms to the prolate side (Fig. 1d), hence also the lowest p-state splits off from the two higher p-states.

By passing we want to mention that when the Na_{14} cluster is heated to 1100 K the time-averaged level density does not any more show a pronounced gap at the Fermi level. At this high temperature cluster shape changes continuously between all shapes and the trajectory in the "shape space" covers uniformly a large area. It should be noted that a free cluster, initially at 1100 K, would very fast cool by evaporation, though evaporation is not observed in our simulations due to the short time scale. Thus it is likely that at experimental temperatures the Na_{14} cluster is strongly deformed also in the liquid state.

In conclusion, we have compared the behaviour of hot "magic" Na_8 and open-shell Na_{14} clusters in ab initio molecular dynamics simulations at elevated vibrational temperatures from 500 to 1100 K, where the ionic structure of all the clusters is completely disordered and exhibits liquidlike diffusion. Na_8 remains magic around 500 K showing a clear electronic shell structure. We find two stable shape isomers (prolate and oblate) for Na_{14} and observe inter-isomeric transitions in our 10 ps time scale for clusters around 600 K. We demonstrate a "dynamical Jahn-Teller effect" in a spherical isomer of Na_{14} where the Fermi level initially lies in the middle of the 1d-2s manifold, but once the dynamics is turned on, the cluster opens a gap at ϵ_F , which stabilizes the deformation to the prolate shape.

ACKNOWLEDGMENTS

We wish to thank Robert N. Barnett and Uzi Landman at Georgia Institute of Technology, Atlanta, for illuminating discussions on the ab initio MD method and for sharing the computer codes. This study is supported by the Academy of Finland. Calculations have been performed at the Center for Scientific Computing, Espoo, Finland, and at the Florida State University Computing Center.

REFERENCES

- [1] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
- [2] M. Brack, Rev. Mod. Phys. **65**, 677 (1993).
- [3] K. Clemenger, Phys. Rev. B **32**, 1359 (1985); W. Ekardt and Z. Penzar, Phys. Rev. B **43**, 1322 (1991); S. Frauendorf and V. V. Pashkevich, Z. Phys. D **26**, S98 (1993); A. Bulgac and C. Lewenkopf, Phys. Rev. Lett. **71**, 4130 (1993); C. Yannouleas and U. Landman, Phys. Rev. B **51**, 1902 (1995); B. Montag, Th. Hirschmann, J. Meyer, P.-G. Reinhard, and M. Brack, to be published.
- [4] G. Lauritsch, P.-G. Reinhard, J. Meyer, and M. Brack, Phys. Lett. A **160**, 179 (1991).
- [5] M. Koskinen, P.O. Lipas, and M. Manninen, to be published.
- [6] J. Martins, J. Buttet, and R. Car, Phys. Rev. B **31**, 1804 (1985).
- [7] U. Röthlisberger and W. Andreoni, J. Chem. Phys. **94**, 8129 (1991).
- [8] V. Bonačić-Koutecký, P. Fantucci, and J. Koutecký, Chem. Rev. **91**, 1035 (1991).
- [9] D. M. Lindsay, Y. Wang, and T. F. George, J. Chem. Phys. **86**, 3500 (1987).
- [10] A. Yoshida, T. Døssing and M. Manninen, J. Chem. Phys. **101**, 3041 (1994).
- [11] G. Ripka, Adv. Nucl. Phys. **1**, 183 (1968).
- [12] K. Selby, V. Kresin, J. Masui, M. Vollmer, W. A. de Heer, A. Scheidemann, and W. Knight, Phys. Rev. B **43**, 4565 (1991).
- [13] J. Borggreen, P. Chowdhury, N. Kebaili, L. Lundsberg-Nielsen, K. Lützenkirchen, M. B. Nielsen, J. Pedersen and H. D. Rasmussen, Phys. Rev. B **48**, 17507 (1993).
- [14] T.P. Martin, U. Näher, H. Schaber, and U. Zimmermann, J. Chem. Phys. **100**, 2322 (1993).
- [15] K. Hansen and J. Falk, to be published.

- [16] M. Brack, O. Genzken, and K. Hansen, Z. Phys. D **21**, 65 (1991).
- [17] For the method, see R. N. Barnett and U. Landman, Phys. Rev. B **48**, 2081 (1993), and for recent applications, see Refs. 28-31 therein and Ref. [20] of this paper.
- [18] Since we allow fractional occupation numbers calculated from a Fermi distribution (with a preassigned electronic temperature $T_{el} \approx 300$ K) in situations where the Kohn-Sham eigenstates are (nearly) degenerate at the Fermi surface (Ref. [17]), the conserved quantity in the MD simulation is the free energy $\Omega = U - T_{el}S$, where U is the total internal energy of the electron-gas system, and S is the entropy of the non-interacting electron gas. [See e.g. R. M. Wentzcovitch, et. al., Phys. Rev. B **45**, 11372 (1992).] The relative fluctuations of Ω are smaller than 0.003% (at $T \approx 600$ K) throughout our simulations, when a time step of 5.2 fs is used.
- [19] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991). The pseudopotential for sodium has been generated and tested by us previously in simulations of sodium chloride clusters, see Ref. [20].
- [20] H. Häkkinen, R. N. Barnett and U. Landman, Europhys. Lett. **28**, 263 (1994); Chem. Phys. Lett. **232**, 79 (1995).
- [21] *CRC Handbook of Chemistry and Physics*, ed. R.C. Weast (CRC Press, Boca Raton 1986); K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York 1979).
- [22] The initial velocities to ions are given such that the components of linear and angular momenta are zeroed. Hence, we calculate the temperature of the cluster as $T = 2E_k/(3N - 6)k_B$, where E_k is the total kinetic energy of ions, N number of ions, and k_B Boltzman constant.
- [23] S. J. Larsson, C. Roxbergh, and A. Lodding, Phys. Chem. Liq. **3**, 137 (1972); G.-X. Qian, M. Weinert, G. W. Fernando, and J. W. Davenport, Phys. Rev. Lett. **64**, 1146

(1990).

FIGURES

FIG. 1. Time evolution of the cartesian moments of inertia of liquid sodium clusters. (a) Na_8 at 550 K, (b) prolate Na_{14} at 650 K, (c) oblate Na_{14} at 610 K, (d) Na_{14} at 480 K started from a spherical shape. For each cluster we show the trajectory in the phase space and the three moments of inertia (in units of $10^3 (\text{amu})a_0^2$) as a function of the time in ps (inset). Note the transition from the prolate shape to oblate shape (and back) in (b), and the rapid strong deformation in (d).

FIG. 2. Evolution of single-electron eigenvalues (in eV) as a function of time in ps (left) and the time-averaged density of states (in arbitrary units, right) in (a) Na_8 at 550 K, (b) prolate Na_{14} at 650 K, (c) oblate Na_{14} at 610 K, (d) Na_{14} at 480 K started from a spherical shape. Note the gap opening at ϵ_F in (d).